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Problems related to the commercial production of levulose

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NOTE TO USERS

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PROBLEMS RELATED TO THE COMMERCIAL PRODUCTION OF LEVULOSE

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PROBLEMS RELATED TO THE COMMERCIAL PRODUCTION OF LEVULOSE

INTRODUCTION

Levulose or d-fructose ($C_6H_{12}O_6$), although possessing properties which should make it more valuable than the ordinary sugars of commerce, has not yet been produced on a commercial scale. The publication by McGlumphy (1) of an improved process incorporating several economic advantages should hasten the time when levulose will be available in commercial quantities at attractive prices. Erb (2) reports that "the commercial preparation of fructose (levulose) is rapidly improving", and predicts that "fructose will some day replace cane sugar in the diet of man."

The distinctive properties (3) which make levulose of commercial interest are its high degree of sweetness (4), great solubility (5), and unique physiological properties. Daniel (6) states that levulose is assimilated to a larger extent and

1. McGlumphy, Problems related to the commercial production of levulose. Ph. D. thesis, Iowa State College, Ames, Iowa. (1930)
2. Erb, Physiological Chemistry. The Chemical Publishing Co., Easton, Penn., p. 49 (1918)
3. For a complete discussion of the properties of levulose see McGlumphy, op. cit., (Reference 1)
4. Biester, Wood and Wahlin, Amer. J. Physiol., 73:387 (1925) report levulose to be 1.73 times as sweet as sucrose.
5. Jackson, Silsbee and Proffitt, U.S. Bur. Standards Sci. Papers, 519:614 (1926) report 375 g. levulose soluble in 100 g. water at 20°C.

oxidized more quickly and in larger amounts per time interval than sucrose. Joslin (7) and many others have found levulose to be of great value in the treatment of diabetes.

When the study of the preparation of levulose from the Jerusalem artichoke (Helianthus tuberosus) was undertaken at Iowa State College, it was found that very little information was available regarding the conversion of the inulin and levulins to levulose. Considerable work was available concerning the hydrolysis of pure inulin, but this was of no value since the process adopted required the direct conversion of all the polysaccharides, rather than the preliminary isolation of the inulin.

The purpose of this paper is to present experimental data designed to show the relations between the factors controlling the conversion process and thus make it possible to convert large batches of artichoke juice conveniently and economically.

Information obtained from the desiccation of two and a half tons of artichoke tubers is included, together with designs for several new pieces of equipment for use in the semi-commercial production of levulose.

6. Daniel, Chem. Zeit., 45:4 (1921)
7. Joslin, Diabetic metabolism with high and low diets, Carnegie Inst. Pub., 323:211 (1923)

CONVERSION OF JERUSALEM ARTICHOKE JUICES

A. Historical

Crookewitt (8) (1843) was apparently the first to convert a polysaccharide to levulose. He observed that inulin will, upon heating 15 hours in water solution, decompose, yielding an uncrystallizable sugar.

Soubeiran (9) (1843) observed that dextrose was not the sole product of the hydrolysis of sucrose. He noted the presence of a levo-rotary sugar which also fermented readily. Biot in a comment appended to Soubeiran's article noted that the speed of a sucrose hydrolysis depended upon the temperature and the amount of acid present. He was apparently the first to study the conditions responsible for the conversion reaction.

Dubrunfaut (10) (1869) gave in detail his technique for the separation of levulose from dextrose as the calcium levulate. He started with 100 c.c. of sirup containing ten grams of previously inverted sugar and added at a low temperature 6 grams of powdered calcium hydroxide. The milky precipitate of calcium levulate was filtered off and decomposed with oxalic, sulfuric or carbonic acid. He had apparently made no study of the conversion reaction.

8. Crookewitt, Ann., 45:184 (1843)
9. Soubeiran, J. de Pharm. III 4:347 (1843)
10. Dubrunfaut, Compt. rend., 69:1366 (1869)

Peligot (11) (1880) sought to improve Dubrunfaut's method. He also started with invert sugar, but made no study of the hydrolysis.

Jungfleisch and Lefranc (12) (1880) recommended the use of as small an amount of acid as possible in hydrolyzing sucrose.

Kiliani (13) (1880) obtained levulose by hydrolyzing inulin in water solution. He claimed a 96.7% conversion of inulin to levulose.

Girard (14) (1880) published a method of preparing crystalline levulose which differs little from Dubrunfaut's procedure. He hydrolyzed a 10% sucrose solution (700 grams of sucrose) in seventeen hours at 60°C., with 20 c.c. HCl per liter of solution.

Weizsaeker (15) (1890) described in detail the method of Jungfleisch because of the difficulties encountered by some in the preparation of crystalline levulose. One hundred grams of very pure sucrose were inverted by boiling precisely five minutes in a liter of distilled water containing a gram of concentrated sulfuric acid. The solution was cooled immediately

11. Peligot, Compt. rend., 90:153 (1880)
12. Jungfleisch and Lefranc, Bull. soc. chim., II, 34:675 (1880), J. pharm. chim., V, 4:437 (1880), Compt. rend., 93:547 (1880)
13. Kiliani, Ann., 205:145 (1880)
14. Girard, Bull. soc. chim., I, 33:154 (1880)
15. Weizsaeker, J. fabr. sucre, 34 (1890). Cited in Harding, Sugar, 25:406 (1923). Original article not examined.

to 32°C. and neutralized by the addition of fifty grams of hydrated lime.

Wiechmann (16) (1891) reported the preparation of some levulose from inulin after hydrolysis with sulfuric acid.

In 1905 the Levulose Company of England (17) secured a patent on a process for preparing inulin and levulose. The pulped raw material was heated to 50 - 70°C. to dissolve out the inulin, taking care to keep the solution neutral, filtering, freeing from albuminoids by centrifuging, recovering inulin by freezing, and finally transforming it into levulose by acid hydrolysis.

Colin (18) (1918) reported that Dubrunfaut, in 1867, noted that artichoke juice in October was levorotary while the following March it was dextrorotary. The levulosans differ profoundly from the primitive inulin by a smaller rotatory power, and by the readiness with which they are hydrolyzed by invertase and yeast. In the alcohol industry, artichoke juices extracted in October should be hydrolyzed by acids, while in the spring, they can be fermented at once.

Wolff and Geslin (19) (1920) published a paper in which they considered some of the properties of inulin and changes

16. Wiechmann, Zeit. Rubenz. Ind., 41 (n.f.28):331 (1891)
17. Levulose Co. of Eng., British Patent 353,670 (1905) Chem. Abstr., 1:1075 (1905)
18. Colin, Compt. rend., 166:305-307 (1918)
19. Wolff and Geslin, Bull. soc. chim. biol., 2:19 (1920)

in its physical state. Inulin prepared from chicory or dahlias was found to be more soluble in water than that obtained from other sources after it had been precipitated by alcohol. It could be converted into the less soluble form by evaporating the solution. The change was apparently reversible and was not fully understood. The hydrolysis of inulin was considered.

Bourquelot and Bridel (20) (1920) studied the products of fermentative hydrolysis of inulin and concluded that inulin contains fructose but no glucose molecule.

Harding (21) (1922) published an original method for the separation of glucose and levulose from invert sugar. By using glacial acetic acid as a solvent, he was able to promote the crystallization of the glucose, while the levulose remained in solution. To obtain the invert sugar, he used the enzyme invertase.

Willaman (22) (1922) suggested the following procedure for the manufacture of levulose sirup.

a. Extraction of juice by diffusion.

b. Clarification by means of lime, phosphoric acid and carbon.

c. Acid hydrolysis of all the inulin bodies.

d. Precipitation of calcium fructosate.

20. Bourquelot and Bridel, Compt. rend., 172:946 (1921)
21. Harding, J. Am. Chem. Soc., 44:1765 (1922)
22. Willaman, J. Biol. Chem., 51:275 (1922)

e. Decomposition of calcium fructosate and evaporation of the fructose solution to sirup.

Jackson, Silsbee and Proffitt (23) (1924) announced that white crystalline fructose had been prepared from the Jerusalem artichoke by extracting the juice, hydrolyzing with dilute sulfuric acid, neutralizing with lime, filtering, precipitating the calcium fructosate, carbonating, filtering and evaporating the sirup in vacuo to 91% solids, crystallizing in motion, centrifuging and drying.

Hocke (24) (1927) tried the method of Daniel (25) on a factory scale. Chicory roots were cut in a beet slicer and extracted in a diffusion battery at a temperature of 75 - 80°C. to produce a juice containing 12 - 14% dry substance. After liming and treating with sulfur dioxide, inulin was crystallized out in yields of 2 - 8%. The inulin was mixed to a paste with 50% water and 0.1% hydrochloric acid. The paste was heated at 90 - 97°C. for 1½ to 1⅔ hours. When the addition of an equal volume of alcohol gave no turbidity, the hydrolysis was considered complete. After neutralizing with sodium hydroxide to only slight acidity, the solution was treated with "Eponite" and filtered.

Jackson, Silsbee and Proffitt (26) (1926) reported their detailed method for the preparation of levulose from the Jerusalem artichoke and the dahlia. The artichoke juices were con-

verted with acid and the levulose precipitated as the calcium levulate, following closely the method outlined by Willaman (27) in 1922. The dahlia juices were frozen to obtain the inulin, which was converted to levulose sirups of 86 - 90% purity. The velocity constant of conversion of inulin at 100°C. in the presence of 0.0094 N. hydrochloric acid was measured and found to be 0.00641. Velocity constants at three other concentrations of acid were also determined, and by taking the differences between the constants at the varying acidities, the investigators were able to eliminate arithmetically the neutralizing influence of the ash and arrive at an approximate velocity of conversion of ash-free inulin. The value obtained was 0.02, while under similar conditions cane sugar was inverted with a velocity of about 0.27. In other words, they found inulin to be more than thirteen times as resistant to hydrolytic action as cane sugar.

Jackson and his associates were apparently the first to really study the conversion of artichoke juices. They heated 175 c.c. of juice (concentration not given) to 79.8°C. and acidified with 2.0 c.c. of 8.473 N. sulfuric acid. They stated that the resulting mixture was thus somewhat less than tenth normal with respect to sulfuric acid, since an undetermined portion

23. Jackson, Silsbee and Proffitt, J. Ind. Eng. Chem. 16:1250 (1924)
24. Hocke, Z. Ver. deut. Zucherind., 76:821 (1926) Sugar, 29:181 (1927)
25. Daniel, op. cit., (Reference 6)
26. Jackson, Silsbee and Proffitt, op. cit., (Reference 5)
27. Willaman, op. cit., (Reference 22)

of the acid was neutralized by the inorganic constituents of the juice. The mixture was maintained at 79.8°C. and at appropriate intervals of time, portions were removed and polarized. Jackson, Silsbee and Proffitt concluded that the resultant of the various reactions occurring during the conversion process follows substantially the course of a unimolecular reaction. They measured a number of velocity constants which will be mentioned here for comparison with the present data. Table 1 is a summary of their results.

Table 1

Velocities of Conversion of Artichoke Juices Under Varying Conditions of Acidity and Temperature. (28)

(The "apparent" acidities are those which would have been produced in pure water. A portion of the acid in each instance was rendered ineffective by inorganic impurities.)

Temperature °C.	Initial Rotation	Final Rotation	Apparent Normality	Velocity Constant
79.8	+ 0.08	-26.43	0.10 H_2SO_4	0.0137
"	"	"	0.20 "	0.0788
78.2	"	"	0.10 HCl	0.0381
99.0	-2.40	-25.88	0.0294 "	0.00327
"	"	"	0.0516 "	0.02737
"	"	"	0.0667 "	0.1371
"	-1.29	-34.48	0.0240 "	0.0010
"	"	"	0.0462 "	0.00593
"	"	"	0.0571 "	0.0163
"	"	"	0.0676 "	0.0353
"	"	"	0.0773 "	0.0707
"	"	"	0.1041 "	0.3172

28. Jackson, Silsbee and Proffitt, op. cit., (Reference 5)

Jackson and his associates observed that the velocities vary considerably with the composition and concentration of the juice. Their interpretation was that, for a more concentrated juice, a greater amount of acid was rendered ineffective by the inorganic impurities and the velocity constants for given strengths of acid were therefore lower. These investigators stated that "it will undoubtedly be possible to predict with satisfactory accuracy the velocity constants for the respective acidities as a function of the concentration of the solution measured either by density or rotary power."

The above investigators performed several experiments to determine the destructive effect of sulfuric acid at temperatures of 70 and 100°C. on levulose. Their results, presented in Table 2, indicate some destruction of levulose.

Table 2

The Decomposition of Levulose in the Presence of Sulfuric Acid (28)

Temperature °C.	Time Minutes	Apparent Normality	Polarization °Ventzke
		(control)	86.25
100	15	0.0304	83.70
"	30	0.0304	82.90
"	15	0.0584	83.30
"	30	0.0584	81.16
		(control)	85.89
70	15	0.0474	85.87
"	30	0.0474	85.63
"	15	0.0891	85.79
"	30	0.0891	85.26

Schering (29) obtained patents on the treatment of an aqueous pulp of inulin with a volatile organic acid such as formic, acetic or carbonic, decolorizing the sirup with charcoal and concentrating to obtain the levulose direct. When carbon dioxide is used, the process is carried out in autoclaves.

Arsen (30) obtained a number of patents in 1927 covering: the purification of inulin by $Mg(OH)_2$, $Ca(OH)_2$, $CaCl_2$, bone-black and Na_2CO_3; the hydrolysis of inulin by tartaric acid or other acids until the rotation passes through a maximum, decreases, and passes through a second maximum even greater than the first; the obtaining of fructose from inulin by 0.01 N. HCl at 100°C., concentration of fructose sirup from purified inulin by the use of less than 70% water and an organic acid such as tartaric of 0.015 N.

In 1928 Arsen (31) secured two additional patents, the first covering the clarification of inulin bearing juice to form a mixture of inulin and other carbohydrates in solution, hydrolyzing to convert into fructose, and adding an enzyme such as pepsin to remove protein impurities. The second patent

29. Schering, British Patent 272,876 (1926), French Patent 634,363 (1927)
30. Arsen, U.S. Patents 1,616,164; 1,616,167; 1,616,169; 1,616,165; 1,616,172; 1,616,171; 1,616,170; 1,616,166 (1927). Chem. Abstr., 21:1026 (1927)
31. Arsen, U.S. Patents 1,663,233; 1,663,234 (1928) Chem. Abstr., 22:1700 (1928)

covers the hydrolysis of the polysaccharides contained in the residue after inulin has been recovered from the juice, and separating the fructose formed.

Hibbert and Percival (32) (1930) obtained velocity constants for the rate of hydrolysis of inulin at 65°C. 1.172 grams of inulin were dissolved in 100 c.c. of 0.10 N. oxalic acid. The initial rotation was -38.0 and the final rotation -80.0. The mean value of K was 0.000501. They observed that the reaction did not appear to be monomolecular.

McGlumphy (33) (1930) attempted to hydrolize inulin by means of carbon dioxide under pressure, according to the method of Schering (34). At temperatures of 85 - 90°C. and carbon dioxide pressures approaching 200 pounds per square inch, the rotation indicated slight hydrolysis. However, the same results were obtained when no carbon dioxide was used, indicating that the slight hydrolysis was simply due to the moisture and temperature. It will be remembered that Crookewitt (35) hydrolysed inulin by simply heating in water solution for 15 hours.

In another experiment, McGlumphy added 465 c.c. of concentrated hydrochloric acid to 28 liters of artichoke juice. The apparent normality was 0.1923. After the solution had stood for nine hours at room temperature, the rotation was -4.5 at 24°C.

32. Hibbert and Percival, J. Am. Chem. Soc., 52:3995 (1930)
33. McGlumphy, op. cit., (Reference 1)
34. Schering, op. cit., (Reference 29)
35. Crookewitt, op. cit., (Reference 8)

The solution was heated at 80°C. for forty-five minutes, at the end of which time the rotation was -6.4 at 24°C. The solution was heated at 80°C. for an additional 30 minute period and the rotation was found to be constant at -6.4.

B. Experimental

1. Method for Determination of Velocity Constants.

Jackson, Silsbee and Proffitt (36) have shown that the resultant of the various reactions occurring during the conversion process follows substantially the course of a unimolecular reaction. It is, therefore, possible to measure the velocity constants of the rates of conversion of artichoke juices for different conditions of acidity and temperature and for different concentrations and compositions of juice. This furnishes the most satisfactory method of attack for this problem.

Following the usual procedure, a quantity of juice was heated and maintained at the desired temperature. The required quantity of acid was added and portions withdrawn from time to time for polarization. Clarification was accomplished by means of a solution of normal lead acetate, as recommended by Jackson, Silsbee and Proffitt.

Flasks of 500 c.c. capacity were supported in a constant-temperature bath and equipped with stirrers. Three hundred and sixty cubic centimeters of juice was placed in a flask and allowed to heat up to the temperature of the bath (80°C.) Forty cubic centimeters of 0.9495 N. hydrochloric acid was added and at the end of five minutes 10 c.c. of the mixture was removed by means of a pipette and added to 10 c.c. of 0.2 saturated normal lead acetate solution. The sample was cooled rapidly to

36. Jackson, Silsbee and Proffitt, op. cit., (Reference 5)

room temperature by shaking under a stream of water and then filtered through a small filter paper. This procedure gave a very satisfactory clarification and the solution was readily polarized in a 100 mm. tube. At appropriate intervals, other samples were withdrawn, clarified, filtered and polarized.

Table 3 shows the data obtained and the constants calculated, and also gives the same information for a duplicate run. The constants obtained, 0.0137 and 0.0135 respectively, are typical of the checks obtained in other duplicate runs and indicate the precision to be expected in data of this type. It will be noted that although the individual constants may vary as much as four units in the second significant figure, the averages agree closely enough for the purposes of this investigation.

Table 3

Velocity constants for the rate of conversion of artichoke juice (14.4% total solids) with 0.095 N. HCl at 80°C.

Run No.	Time minutes	Rotation observed	$R_t - R_\infty$	Log $\frac{R_o - R_\infty}{R_t - R_\infty}$	$K = \frac{1}{.4343\ t} \log \frac{R_o - R_\infty}{R_t - R_\infty}$	
1	0	+2.2	10.0			
	5	1.5	9.3	0.03152	0.0145	
	20	-0.4	7.4	0.13077	0.0150	
	45	2.5	5.3	0.27572	0.0142	Avg.
	85	4.9	2.9	0.53760	0.0146	0.0137
	120	5.8	2.0	0.69897	0.0135	
	190	6.7	1.1	0.95861	0.0117	
	315	7.6	0.2	1.69897	0.0125	
	∞	7.8				
2	0	+2.0	9.7			
	20	-0.4	7.3	0.12345	0.0143	
	50	2.9	4.8	0.30553	0.0141	
	85	4.4	3.3	0.46826	0.0127	Avg.
	115	5.6	2.1	0.66455	0.0134	0.0135
	185	6.8	0.9	1.03253	0.0129	
	285	7.5	0.2	1.68574	0.0136	
	∞	7.7				

2. Titratable acidities of raw and converted juices.

It was observed by Jackson, Silsbee and Proffitt (36) that for a given concentration of acid the conversion proceeded more slowly in a concentrated juice than in a more dilute juice. They interpreted this as being due to the neutralization of a portion of the acid by the inorganic constituents of the juice. Consequently, in a more concentrated juice, "a greater amount of acid was rendered ineffective by the inorganic impurities and the velocity constants for given strengths of acid are lower".

In order to test this theory, a number of titrations were made and the results are presented in Table 4.

Table 4

Normalities determined by titration with standard NaOH solution, phenolphthalein indicator.

% total solids	7.2	14.4	18.0	26.1
Raw juice	0.0143	0.0238	0.0306	0.0445
Acid added	0.0950	0.0950	0.0950	0.0950
Total	0.1093	0.1188	0.1256	0.1395
Actual titration	0.1020	0.1088	0.1212	0.1292
Difference	0.0073	0.0100	0.0044	0.0103

Because of the coloration of the juices, even when highly diluted, it was difficult to determine the exact endpoint. This is advanced as a possible explanation for the difference between the normality of the converted juice and the sum of the normalities of the raw juice and the acid added. It is hardly pos-

sible that this difference represents the amount of the added acid which is neutralized by inorganic impurities because, if such were the case, this difference would increase regularly with increase in the concentration of the juice. No such regularity is noted in the values of Table 4, and furthermore, one of the more concentrated juices gives the lowest value for this difference.

From these data, we conclude that the actual titratable acidity of a converted juice is practically equal to the initial acidity of the raw juice plus that of the acid added. If any of the acid is "rendered ineffective by inorganic impurities" as claimed by Jackson, Silsbee and Proffitt, it is a negligible quantity. For a given concentration of added acid, the more concentrated juices have a higher titratable acidity than the less concentrated juices, due to the higher initial acidity of the raw juice.

If it is true that a more concentrated juice has a lower velocity constant than a less concentrated juice at the same acidity, it is necessary to look to other factors than the titratable acidity for the explanation.

3. Conversion with hydrochloric acid.

Table 5 gives the velocity constants obtained for the rates of conversion of artichoke juices with hydrochloric acid at 80°C. Two series of determinations were made, in the first the acidity was held constant while the concentration of the juice was varied, while in the second the acidity was varied and the concentration of juice held constant. The pH values of the converted juices were obtained by means of the quinhydrone electrode in the usual manner. Following the manner of Jackson, Silsbee and Proffitt (37), the normality of acid that would be obtained by a corresponding dilution with distilled water is termed the apparent normality. The apparent normality is used and recorded in this work for the reason that it gives the amount of acid actually added to the juice. The data presented later indicate that this information is of more value than the total titratable acidity of the mixture.

37. Jackson, Silsbee and Proffitt, op. cit., (Reference 5)

Table 5

The conversion of artichoke juices with HCl at 80°C.

Juice % Total Solids (refractometer)	Apparent Normality	Velocity Constant	(quinhydrone electrode) pH
7.2	0.095	0.1680	1.68
14.4	"	0.0136	2.80
18.0	"	0.0053	3.19
26.1	"	0.0015	3.83
14.4	0.0475	0.0009	4.10
"	0.0950	0.0136	2.80
"	0.1425	0.0690	2.09
"	0.1900	0.2310	1.55

The first four figures in column 3 show an increase of one hundred-fold in the velocity constant for a juice of 7.2% total solids, as compared with a juice of 26.1% total solids, the apparent normality being constant. This vast difference shows that values of the velocity constants are worthless unless the concentration of the juice is specified. It will be pointed out later that variations in the composition of the juice affect the velocity constants to a much smaller extent. Apparently, Jackson, Silsbee and Proffitt were unaware of the very large difference caused by concentration. They observed that juices of higher concentration were converted more slowly than juices

of lower concentration, but they record their constants without specifying the concentrations of the juices other than to mention that the concentrations are illustrated by the final rotations. Since they do not give the details of their method for clarification or state the type of tube used for polarization, it is impossible to determine the concentration of their juices from the data given.

In the second part of the table, the concentration is held constant while the apparent acidity is varied. It was to be expected that the velocity constant would increase with increase in apparent acidity.

A study of the pH values obtained indicates definitely that the reason for the differences in the velocity constants for different concentrations of juice at the same apparent normality is to be found in the buffer action of certain of the constituents of the raw juice.

4. Conversion with sulfuric acid.

For the conversion of artichoke juices on a large scale of operations, sulfuric acid has a number of advantages which should not be overlooked. In the first place, it is the cheapest of all acids. The cost factor becomes of the utmost importance as soon as the scale of operations begin to approach commercial production. Sulfuric acid has the additional advantage over hydrochloric acid of being precipitated out as the insoluble calcium sulfate when the converted juice is neutralized with hydrated lime. Thus, it does not add to the dissolved impurities as is the case with some of the other acids.

Table 6 gives the results of eight determinations of velocity constants made with varying strengths of sulfuric acid and varying concentrations of juice.

Table 6

The Conversion of Artichoke Juices with H_2SO_4 at 80°C.

Juice % Total Solids (refractometer)	Apparent Normality	Velocity Constant	pH (quinhydrone electrode)
14.4	0.0573	0.0013	3.92
"	0.1147	0.0109	2.77
"	0.1720	0.0513	1.95
"	0.2294	0.1270	1.61
30.8	0.1560	0.0107	2.77
30.7	0.2364	0.0433	1.94
30.6	0.3150	0.0973	1.45
30.5	0.3940	0.2170	1.23

In the second and fifth lines of the above table are to be found constants that are practically identical. It will be noted that the pH values corresponding to these constants are the same, altho one juice contains 14.4% total solids and 0.1147 N. acid while the other contains 30.8% total solids and 0.1560 N. acid. This suggests the possibility that the velocity constant depends only upon the pH of the mixture of acid and juice.

5. Decomposition of levulose during conversion.

Jackson, Silsbee and Proffitt (38) report a decrease in rotation for solutions of pure levulose acidified with sulfuric acid (0.0304 - 0.0891 N.) and maintained at 70 and 100°C. for 15 to 30 minutes. No pH values are given in connection with their work. They conclude that "under any conditions of acidity and temperature which are necessary for the conversion of the inulins, levulose probably suffers more or less destruction."

Just as the conversion of the inulins depends primarily upon the pH value of the solution, so will the destruction of the levulose so formed also depend upon the pH value. Because of the very decided buffer action of certain constituents of the juice of the Jerusalem artichoke, which was demonstrated in sections 3 and 4, it is misleading to compare a run of this type to a conversion experiment having the same apparent acidity. Such comparisons must be on a pH basis.

In order to obtain data concerning the destruction of levulose under certain conditions of pH and temperature, the following experiments were carried out.

Approximately 12 grams of levulose (prepared in this laboratory)were dissolved and diluted to 200 c.c., placed in one of the conversion flasks in the water bath, and brought up to 80°C. Ten c.c. were removed and polarized. One c.c. of 23.6369 N. sulfuric acid was added to the remainder of the 6%

levulose solution, and polarizations made at intervals as shown in Table 7 .

38. Jackson, Silsbee and Proffitt, op. cit., (Reference 5)

Table 7

Decomposition of 6% levulose solution at 80°C. and pH of 1.31

Time minutes	Rotation °Ventzke
0	-11.4
15	-11.4
37	-11.4
120	-11.4
195	-11.4

For the next run, approximately 24 g. of the same levulose was dissolved and diluted to 200 c.c. and 2 c.c. of the 23.6369 N. sulfuric acid was added after 10 c.c. of the original solution had been removed and polarized.

Table 8

Decomposition of 12% levulose solution at 80°C. and pH of 1.12

Time minutes	Rotation °Ventzke
0	-22.0
15	-22.0
45	-22.0
80	-22.0
130	-21.7

The same run was repeated at 90°C.

Table 9

Decomposition of 12% levulose solution at 90°C. and pH of 1.12

Time minutes	Rotation °Ventzke
0	-21.0
15	-18.9
30	-18.3

These data show that, at temperatures up to 80°C. and pH values down to 1.12, the amount of levulose destroyed in 60 minutes is insignificant. The conversion experiments reported so far in this work show that it will never be necessary to exceed these conditions in practical work, since juices of any concentration may be completely converted at pH values above 1.12 in 60 minutes or less.

6. Conversion as a function of pH.

In order to obtain sufficient data to plot a curve showing the relationship between the pH of any acidified artichoke juice and the values of the velocity constants of the rate of conversion, some additional velocity constants were determined. These are presented in Table 10.

Table 10

Conversion of artichoke juices at 80°C.

Apparent acidity	Juice % Total Solids (refractometer)	Velocity Constant	pH (quinhydrone electrode)
0.114 N. H_2SO_4	7.05	0.0766	1.71
0.371 "	26.60	0.1180	1.50
0.0782 N. HCl	7.10	0.0986	1.80
0.175 "	22.30	0.0262	2.49
0.216 "	21.80	0.0984	1.86
0.267 "	23.30	0.1650	1.51

Figure 1 shows the pH values plotted against the velocity constants for all the determinations presented in this work. These data represent various concentrations of juice and acid at a temperature of 80°C., both sulfuric and hydrochloric acids being used. It is evident from the curves, that the velocity constant is a function of pH only for either acid. The fact that the two acids form separate curves is presumedly to be attributed to the relative influences of the negative ions.

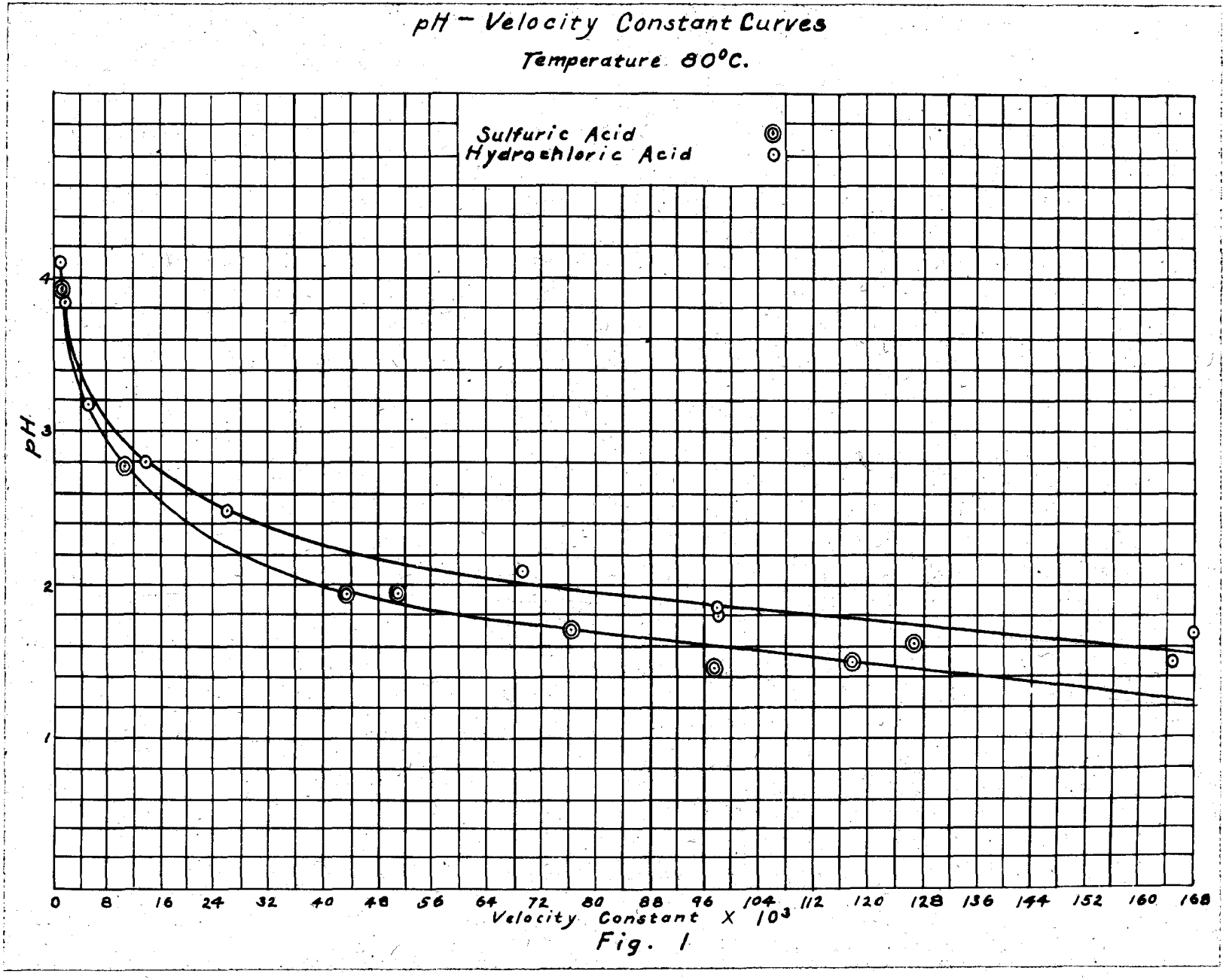
pH – Velocity Constant Curves
Temperature 80°C.
Sulfuric Acid
Hydrochloric Acid
pH
4
3
2
1
0
8
16
24
32
40
48
56
64
72
80
88
96
104
112
120
128
136
144
152
160
168
Velocity Constant X 10³

Fig. 1

7. The technique and control of conversion as a step in the process for the commercial production of levulose from the Jerusalem artichoke.

From a commercial standpoint, it is necessary to know how to completely convert a juice of any concentration or composition in a reasonable time and without the destruction of appreciable quantities of levulose.

The work which has been reported so far was all done on juice prepared from dried artichoke chips. The chips were extracted in a diffusion battery of six to eight cells. The battery was operated in the usual manner so that the fresh water came in contact with the most nearly exhausted chips, while the concentrated juice passed through the fresh chips. In some cases, the juice was obtained from this small diffusion battery, and in other cases, from a similiar procedure using beakers in a water bath. The juice was usually made up fresh for each experiment, the only precaution necessary was to see that the chips were completely exhausted before discarding. Since concordant results have been obtained throughout the work, it is evident that minor differences in composition, such as would be encountered in the day to day operation of a commercial plant, are of no consequence. The discussion of the effect of major differences in composition, such as the use of different varieties of Jerusalem artichokes or different methods for obtaining the juice must be deferred until after the presentation of addition-

al data.

In connection with the semi-commercial production of levulose at Iowa State College, it was desired to convert batches of juice in exactly one hour's time, regardless of the concentration of the juice, in order that the step should fit in as a unit in the whole process. The velocity constant required for 99.9% conversion in sixty minutes may be computed as follows:

$$K = \frac{1}{0.4343\ (60)} \log \frac{1000}{1} = 0.115$$

From the above calculation, we find that a constant of 0.115 is required to convert 99.9% of the juice in sixty minutes. Figure 1 shows that at 80°C. a constant of 0.115 is obtained at a pH of 1.5 when sulfuric acid is used, or at a pH of 1.75 when hydrochloric acid is used.

In order to be able to obtain any desired pH easily, the following series of experiments were carried out.

Several liters of approximately 40% juice was prepared. Dilutions were made so as to give eight different concentrations of juice, from 40% down to 6% total solids. Refractive index measurements were made on each solution and the percent total solids calculated therefrom.

Solutions of sulfuric and hydrochloric acid, approximately 2 normal, were prepared and standardized by titration with a standard sodium hydroxide solution, using phenolphthalein indicator.

The method of procedure was to take 20 c.c. of juice and add a quantity of acid solution and sufficient water to make the total volume 25 c.c. After thorough mixing, the pH of the solution was determined, using the quinhydrone electrode in the usual manner. For each concentration of juice, three or four different proportions of the acid were used, care being taken to include pH values both lower and higher than the 1.5 - 1.75 range in which we were interested.

The data obtained when sulfuric acid was used are presented in Table 11. The first column shows the concentration of the juice after dilution with acid and water, since in commercial work concentrated acids would be used and the amount of dilution would be insignificant. The normalities given were calculated from the amount of acid added and correspond to the apparent normalities used elsewhere in this work. The reason for the use of apparent normalities is obvious. We are interested in the amount of acid that has actually been added to the juice, not in the total titratable acidity of the juice. It was pointed out in section 2 that values of the total titratable acidity were of no value in connection with the velocity constants of the rate of conversion.

Table 11

Normality-pH data for Different Concentrations of Juice Treated with Sulfuric Acid. (Acid used, 2.3955 N. H_2SO_4)

Juice %T.S.		A	B	C	D
	c.c. acid	1.06	2.00	0.50	1.50
	Normality	0.1016	0.1916	0.0479	0.1437
4.8	E.M.F.	0.3233	0.3420	0.2804	0.3342
	pH	1.62	1.31	2.36	1.45
	c.c. acid	1.00	2.00	1.50	
	Normality	0.0958	0.1916	0.1437	
8.65	E.M.F.	0.2973	0.3357	0.3240	
	pH	2.07	1.42	1.61	
	c.c. acid	1.02	3.02	2.00	
	Normality	0.0977	0.2894	0.1916	
12.8	E.M.F.	0.2644	0.3430	0.3242	
	pH	2.62	1.29	1.61	
	c.c. acid	2.00	3.00	2.50	
	Normality	0.1916	0.2875	0.2396	
16.7	E.M.F.	0.3090	0.3372	0.3265	
	pH	1.87	1.40	1.57	
	c.c. acid	2.00	4.00	3.00	
	Normality	0.1916	0.3833	0.2875	
19.9	E.M.F.	0.2916	0.3446	0.3284	
	pH	2.16	1.27	1.54	
	c.c. acid	3.00	4.00	3.50	
	Normality	0.2875	0.3833	0.3354	
23.0	E.M.F.	0.3187	0.3415	0.3328	
	pH	1.71	1.32	1.46	
	c.c. acid	4.00	3.00	5.00	
	Normality	0.3833	0.2875	0.4791	
25.5	E.M.F.	0.3339	0.3075	0.3470	
	pH	1.45	1.90	1.23	
	c.c. acid	5.00	4.00	4.50	
	Normality	0.4791	0.3833	0.4312	
34.2	E.M.F.	0.3350	0.3142	0.3255	
	pH	1.43	1.79	1.59	

Another series of experiments were performed in which hydrochloric acid was substituted for sulfuric acid. The results are presented in Table 12.

Table 12

Normality-pH data for different Concentrations of Juice Treated with Hydrochloric Acid (Acid used, 1.920 N. HCl)

Juice %T.S.		A	B	C
	c.c. acid	1.00	2.00	0.50
	Normality	0.0768	0.1536	0.0384
4.8	E.M.F.	0.3250	0.3512	0.2694
	pH	1.60	1.16	2.54
	c.c. acid	2.00	3.00	1.00
	Normality	0.1536	0.2304	0.0768
12.8	E.M.F.	0.3272	0.3524	0.2370
	pH	1.56	1.13	3.09
	c.c. acid	3.00	4.00	2.00
	Normality	0.2304	0.3072	0.1536
19.9	E.M.F.	0.3315	0.3562	0.2730
	pH	1.49	1.07	2.48
	c.c. acid	5.00	3.00	4.00
	Normality	0.3840	0.2304	0.3072
25.5	E.M.F.	0.3603	0.2966	0.3400
	pH	1.00	2.08	1.35

In order to make use of the information contained in Tables 11 and 12, it is necessary to plot a series of curves showing the relation between the apparent normality and pH values for each concentration of juice. The data for sulfuric acid are plotted in Figure 2, while Figure 3 shows similiar curves for hydrochloric acid.

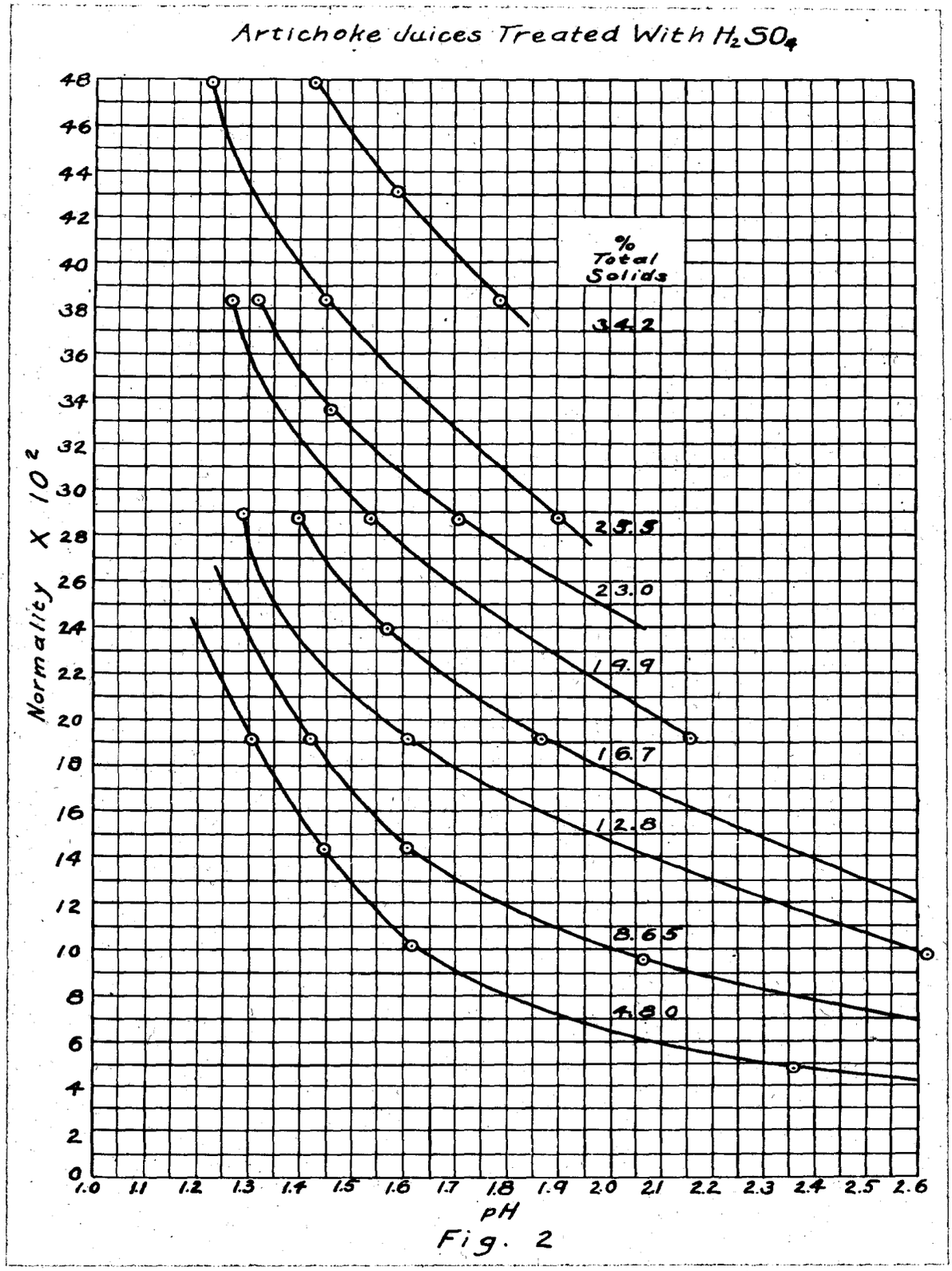
Artichoke Juices Treated With H_2SO_4
Normality X 10^2
pH
% Total Solids
34.2
25.5
23.0
19.9
16.7
12.8
8.65
4.80
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
44
46
48
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
2.6

Fig. 2

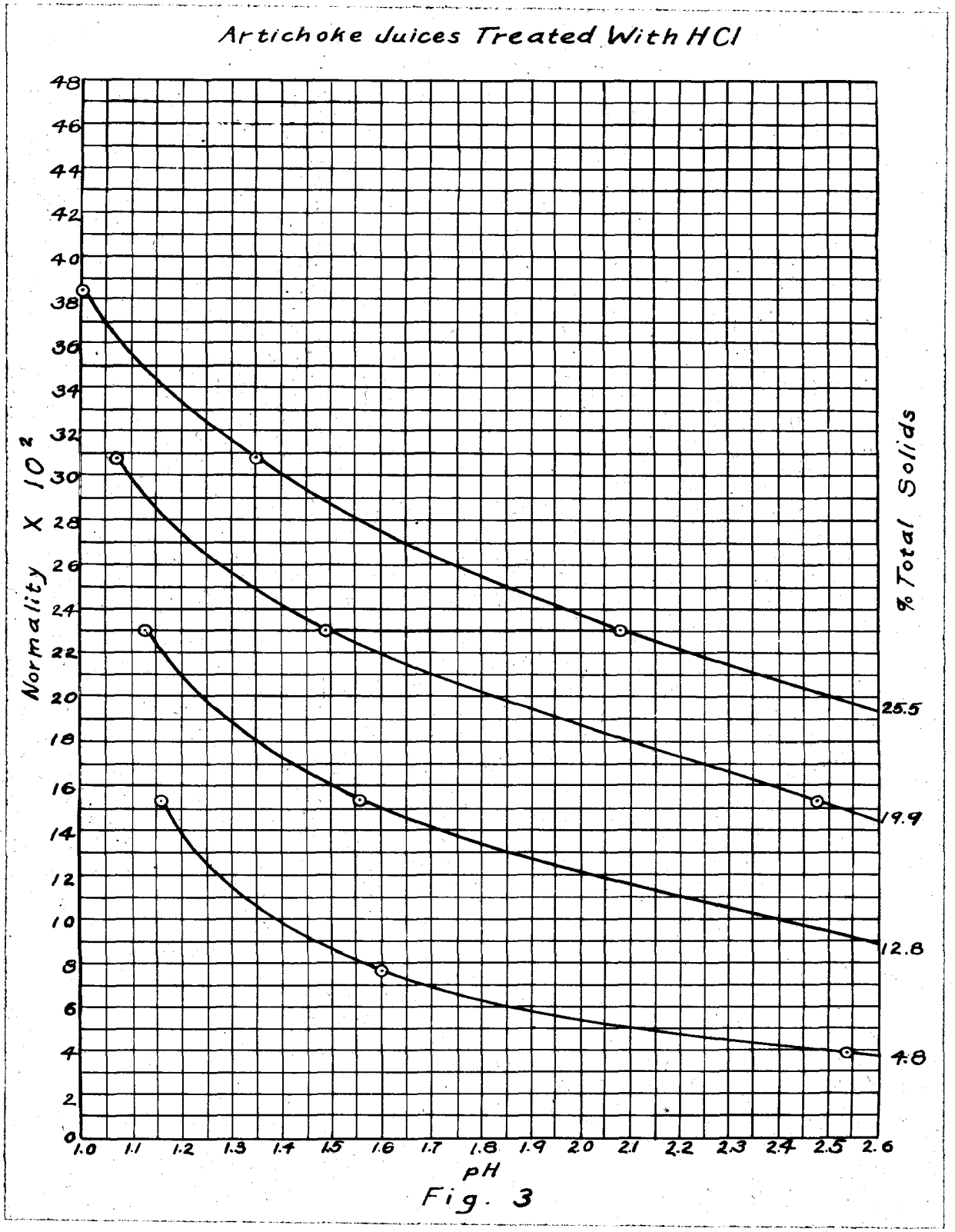
Artichoke Juices Treated With HCl
Normality X 10²
% Total Solids
pH
25.5
19.9
12.8
4.8
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
2.6

Fig. 3

From the curves of Figure 2, the normalities corresponding to pH values of 1.5 were obtained by interpolation. When these normalities were plotted against the corresponding concentrations of juice, a straight line was obtained. In other words, we have found that the amount of acid required to produce a definite pH is directly proportional to the concentration of the juice, as measured by the refractive index.

By interpolation and extrapolation, we may compute the amount of acid required to produce a pH of 1.5 for a juice of any concentration. Table 13 shows the values for apparent normality thus obtained. The data for hydrochloric acid were treated in the same manner, and the third column of Table 13 gives the values for the apparent normalities required to produce a pH of 1.75 by the use of hydrochloric acid.

Table 13

Apparent Normality of Acid Required for 99.9% Conversion in One Hour at 80°C. (The "apparent" normalities are those which would have been produced in pure water.)

% Total Solids	Apparent Normality H_2SO_4	Apparent Normality HCl	% Total Solids	Apparent Normality H_2SO_4	Apparent Normality HCl
4	0.120	0.058	23	0.332	0.238
5	0.131	0.067	24	0.343	0.248
6	0.142	0.077	25	0.354	0.257
7	0.153	0.086	26	0.365	0.267
8	0.164	0.096	27	0.376	0.276
9	0.175	0.105	28	0.388	0.286
10	0.187	0.115	29	0.399	0.295
11	0.198	0.124	30	0.410	0.305
12	0.209	0.134	31	0.421	0.314
13	0.220	0.143	32	0.432	0.324
14	0.231	0.153	33	0.443	0.333
15	0.242	0.162	34	0.454	0.343
16	0.254	0.172	35	0.465	0.352
17	0.265	0.181	36	0.476	0.362
18	0.276	0.191	37	0.487	0.371
19	0.287	0.200	38	0.498	0.381
20	0.298	0.210	39	0.509	0.390
21	0.309	0.219	40	0.521	0.400
22	0.321	0.229			

It is now a very simple matter to convert any juice in one hour at a temperature of 80°C. without the destruction of a measurable amount of the levulose. The juice is prepared and the refractive index measured. By consulting a table (39), the percent total solids is found. From Table 13, we find the proper amount of sulfuric or hydrochloric acid to be added.

39. Van Nostrand's Chemical Annual. D. Van Nostrand & Co., New York, p. 615 (1926)

8. Effect of major differences in composition.

A quantity of juice was prepared by soaking dried artichoke chips in hot water for forty-five minutes and pressing out the juice with a small screw press. This procedure should produce a juice of different composition because much of the soluble material, which is removed by the diffusion process, remained in the pulp. Since the solubilities of the extractable components of the artichokes are different, any process that does not completely extract the artichokes will produce a juice with a higher percentage of the more soluble constituents and a correspondingly lower percentage of the less soluble constituents. Such a juice would exhibit a different buffer action, and a different quantity of acid would be required to convert it.

The refractive index of the solution was determined and corresponded to a concentration of 19.6% total solids. According to Table 13, an apparent normality of 0.292 with sulfuric acid should produce a pH of 1.5 and a velocity constant of 0.115. The pH was found to be 1.29, while the velocity constant was 0.234.

Another portion of the juice was treated with hydrochloric acid. The resulting solution had a concentration of 15.8% total solids, while the apparent normality was 0.194. It was calculated from Figures 3 and 1 that an apparent normality of 0.194 with hydrochloric acid in a juice whose concentration is 15.8% total solids, should produce a pH of 1.5 and a velocity constant

around 0.170. The pH was found to be 1.3, and the velocity constant was 0.283.

In the above experiments, instead of obtaining pH values of 1.5, we obtained values of 1.29 and 1.3 respectively. With either hydrochloric or sulfuric acid, the value is practically 0.2 of a pH unit lower than for juice obtained in the ordinary manner. This shows that a juice obtained by a method that does not completely extract the chips has less buffer action than a juice of the same concentration obtained by the regular methods. For this reason, the data of Tables 9 and 10 will not apply to such juices.

The curves of Figure 1 were extended and it was found that points representing the data of the above experiments did not fall on the curves, but considerably below them, thus showing that a lower pH was required for a given value of velocity constant. The law of mass action would anticipate such a result, since the concentration of inulin and levulins is proportionately lower in such a juice. This means that the curves of Figure 1 cannot be used in connection with juices having a composition considerably different from the juices used for obtaining the data.

These conclusions can be expected to apply equally well in the case of different varieties of artichokes, which would yield juices of different composition.

In the case of major differences in composition, then, it is necessary to obtain new data, and prepare new graphs showing the relationship between pH and the velocity constants, and between pH and the apparent normalities.

C. Discussion

To develop a process from laboratory scale to commercial production is usually a difficult undertaking. This statement is especially true of the levulose problem. Levulose is a product that would be of great value to humanity if its large scale production could be accomplished. During the past fifty years, many attempts have been made to solve this problem, but the fact that levulose is only available in small quantities and at high prices shows the failure of these efforts.

An improved process has been developed at Iowa State College which embodies some important economic advantages. Details of the process have been given by McGlumphy (40), and the work of adapting it to semi-commercial production is under way. During the past year, many problems have arisen in connection with this work. Some of these problems were quickly solved, but others have required an extended investigation. Of the latter, the matter of the conversion of the substances of the inulin group, together with the small amount of sucrose contained in artichoke juices, was one of the first to come to our attention.

The optimum conditions for the conversion of artichoke juices were not determined by previous investigators. The underlying factors of the process were little understood, and even in the most recent and complete work, unjustified assumptions

40. McGlumphy, op. cit., (Reference 1)

were made which caused the investigators to overlook a most important factor.

It is interesting to note that, although the conversion reaction is undoubtedly of a high order, the resultant of the various reactions follows substantially the course of a unimolecular reaction. The present data are in accord with those of Jackson, Silsbee and Proffitt (41) on this point.

It is difficult to understand why previous investigators, especially those of recent years, have always approached the problem from the standpoint of titratable acidity, rather than hydrogen-ion concentration. The various sugars and complex polysaccharides are known to exhibit buffer action, and the inversion of sucrose has long been known to depend on hydrogen-ion concentration or, more accurately, on hydrogen-ion activity.

The failure of pH-velocity constant data for sulfuric and hydrochloric acids to fall on the same curve indicates a difference in the action of the negative ions on some of the constituents of the juice. It is possible that molecular combinations are formed between the ions and certain constituents of the juice. This phase of the problem will require more work before these relations are understood.

The present data concerning the decomposition of levulose under conditions of high acidity and temperature apparently do

41. Jackson, Silsbee and Proffitt, op. cit., (Reference 5)

not agree with those of Jackson, Silsbee and Proffitt (41), altho they are not exactly comparable. A possible explanation of this lies in the levulose used in our work. A rather crude, yellow colored levulose obtained from sirups that had been allowed to crystallize by abandonment was used in order to more nearly approximate conditions in the raw juice. Certain of the impurities in the mother liquor were present, and might well have provided a certain protective influence. In any event, the data obtained are more to the point than if highly purified levulose had been used, and they are substantiated by the fact that many of the converted juices were maintained at 80°C. for long periods of time without showing loss in rotation.

More data regarding the rate of conversion of juices of varying compositions are desirable. The data at hand indicate that the error which would result from using the data of Table 13 for the conversion of a juice of different composition would be slight, and on the side of safety. A few determinations of velocity constants and pH values would readily show whether or not these data could be applied to a juice of unknown composition.

DESICCATION OF JERUSALEM ARTICHOKE TUBERS

McGlumphy (42) made a study of the desiccation of Jerusalem artichoke tubers and the use of the dried chips for the production of levulose. He found a number of advantages were obtained when the desiccation process was employed, and presented a design for a continuous drier. This drier has been built and operated and a summary of the results obtained will be presented.

The continuous drier consists of a screw conveyor, six inches in diameter and ten feet in length, supported in a galvanized iron trough. A wire screen through which hot air can be passed is supported directly under the screw, and the sliced tubers are carried along the screen by the screw. The trough is divided into three sections, each with a pipe connection through which hot air may be admitted. McGlumphy found that temperatures up to 125°C. may be employed during the first stages of the desiccation process without harming the product, but that the temperature must be reduced to 80°C. or less during the last stages of the process. The division of the trough into three compartments permits the use of different temperatures at different stages of the desiccation process. A mechanical slicer is attached to the inlet end of the trough, and the sliced tubers are fed directly into the screw. A mechanical arrangement

42. McGlumphy, op. cit., (Reference 1)

permits the screw to be operated at different speeds so that the time of drying may be adjusted when necessary. The air is supplied by a Buffalo volume fan operating at 3600 R.P.M. and supplying 720 cubic feet of air per minute. The air heater consists of a bank of 36 10-foot sections of one-inch pipe enclosed in a galvanized iron box. The fan is placed directly under one end of the heater and blows the air up into the box where a system of baffles causes it to pass up and down over the pipes several times during its passage through the box. A number of openings are provided along the side of the heater box, and various temperatures of air (50 - 127°C.) may be obtained, depending upon which openings are used.

After a few preliminary trials, satisfactory operation of the unit was obtained, and about fifty bushels of Jerusalem artichoke tubers were desiccated with this equipment. The details of a typical run are presented.

Two bushels of tubers were dried in two hours and forty minutes. The average temperatures were as follows; 115°C. in the first compartment, 112°C. in the second compartment, and 85°C. in the last compartment. The average static pressure in the heater box was 4 inches of water, as measured by a manometer. A sample of the dried chips was analysed and showed 5.80% moisture.

McGlumphy made a number of sugar analyses on both fresh

and dried tubers and concluded that the desiccation process, when properly carried out, did not destroy an appreciable amount of the sugars present. In order to determine whether the above drying procedure was satisfactory in this regard, analyses were made on a sample of the dried chips and on fresh tubers from the same baskets of artichokes. The sugars were determined by Ost's cupro-carbonate method as modified by Nyns (43). The following results were obtained.

	Dried chips	Fresh tubers
% levulose (dry basis)	65.97	64.43
% glucose " "	12.85	12.40

The slightly higher values for the sugars in the dried chips indicate nothing more than the shortcomings of the method of analysis. The values check as well as may be expected from experience in this laboratory with Nyns' method of analysis, and we conclude that no appreciable amount of sugar has been destroyed by the desiccation process.

One difficulty was encountered in the operation of the continuous drier. When the sliced artichoke tubers were partially dry, they became somewhat sticky and tended to ball together. This necessitated occasional stirring throughout the trough to break up the clumps. After the clumps were broken up and the drying had progressed further, no more trouble was encountered. The chips were carried along nicely by the screw and were dis-

43. Nyns, Bull. assoc. école sup. brasserie Louvain, 25:63 (1925); Chem. Abstr., 19:1236 (1925)

charged from the end of the trough in a continuous stream.

In order to determine the effectiveness of a tray drier for the desiccation of artichoke tubers, the following trial was made. A wooden box two feet wide, three feet long and two feet deep was equipped with a false bottom of wire screen placed about nine inches from the top of the box. A bushel of sliced tubers were placed on the screen, and hot air at a temperature of 125°C. was admitted into the bottom of the box. The static pressure in the heater box was equivalent to six inches of water. The drying was continued for an hour and a half, at the end of which time it was found that the chips at the bottom and sides of the box were too brown, while those in the center were not completely dried. There was a tendency for the mass to pull away from the sides as the drying progressed. This indicated that some stirring would be necessary for the successful drying of artichoke slices with a tray drier. Furthermore, previous experience indicated that the temperature should be lowered as the drying progressed.

Some further experimental work was done using several trays operated at decreasing temperatures and transferring the chips from tray to tray. The final arrangement consisted of two trays like the one described above and a third tray somewhat deeper than the others and divided into two sections. The average temperature in the first tray was 108°C, while the second and

third trays were maintained at about 95°C. and 73°C. respectively. A large square of cloth was placed in each tray to aid in transferring the chips. The cloth was large enough that a considerable margin hung over the sides of the tray, and the corners could be gathered together to lift out the chips. A bushel of sliced tubers were placed in the first tray and allowed to remain forty-five minutes. At the end of this time, they were lifted out by means of the cloth and dumped into the second tray in such a manner that the mass was inverted and the chips that had been on the top of the first tray were on the bottom of the second tray. The first tray was refilled with fresh slices and the drying continued for another forty-five minutes. From the second tray, the chips were transferred to the first section of the third tray, and finally to the second section of the third tray. Each batch of chips was thus subjected to the action of hot air for a period of three hours, during which time the temperature was dropped from 108°C. to 73°C. The three transfers thoroughly mixed the chips so that uniform drying was obtained. The moisture content of the chips dried in this manner varied from 4% to 6%. The process was quite satisfactory and about sixty bushels of Jerusalem artichoke tubers were desiccated by means of this equipment.

It would be relatively simple to construct a drier of this type in which the trays were automatically dumped at the end of

each drying period. Another possible modification would be to employ drying trays for the first stages of the process and transfer the chips to the continuous drier when they were no longer sticky.

DESIGN OF EQUIPMENT

A. Continuous Extraction Unit

There are many advantages to be gained by making a process or a step in a process continuous. The more important advantages are a more uniform product, less labor expense, and better control. Many industries have changed over from the old batch methods to continuous processes, but there are very few cases where this has been done in the sugar industry.

In the design of equipment for the semi-commercial production of levulose, we wish to utilize the advantages of the continuous process as much as possible. With this policy in mind, an apparatus has been designed which will materially decrease the amount of labor and attention required for the extraction or diffusion of the dried artichoke chips.

A diagramatic sketch of the continuous extraction unit is shown in Figure 4. The cells of the ordinary diffusion battery are replaced by a number of cups fastened to an endless chain. A tube reaches from the bottom of each cup to an opening in the side, near the top. This allows the liquid from the bottom of the cup to overflow and run down the chain into the next cup. A suitable screen is placed in the bottom of each cup to prevent the tube from becoming clogged. The artichoke chips are fed into the tank, either automatically or by hand. Each cup, as it passes through the bottom of the tank, is filled with

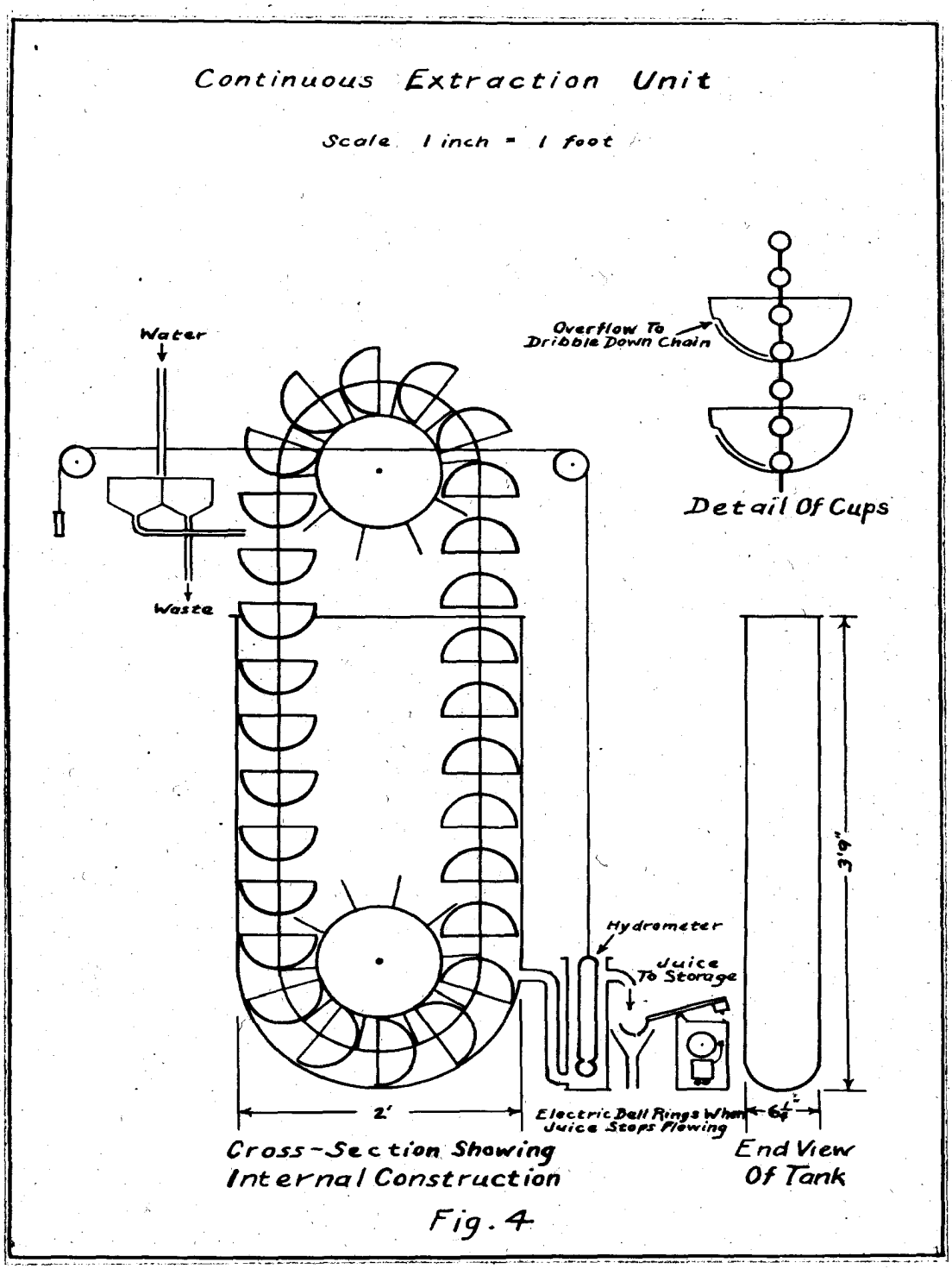
Continuous Extraction Unit
Scale 1 inch = 1 foot
Water
Waste
Overflow To Dribble Down Chain
Detail Of Cups
Hydrometer
Juice To Storage
2'
Electric Bell Rings When Juice Stops Flowing
6½"
3'9"
Cross-Section Showing Internal Construction
End View Of Tank

Fig. 4

chips. The chips are carried up through the tank and are dumped as the cups pass over the upper wheel. The water passes down through the chips by gravity, being transferred from the bottom of one cup to the top of the cup directly underneath. By the use of the overflow tube, the cups are full of water at all times, thus assuring effective diffusion. The concentrated juice collects in the bottom of the tank where it is in direct contact with the fresh chips being fed into the apparatus.

An automatic water control is shown in connection with the continuous extraction unit in Figure 4. The concentrated juice is drawn off through an opening near the bottom of the large tank. The juice then passes in the bottom and out the top of an open cylinder containing a large hydrometer. A slight movement of the hydrometer will swing the small rubber tube admitting the water, and cause the water to be wasted to the sewer or run into the cups as required.

Another automatic feature of this design is the electric warning signal. This consists of a lever with a small cup at one end and a counterweight and an electric contact at the other end. The cup has a small hole in the bottom so it will drain quickly when the flow of juice stops. This hole is small enough so the cup is running over as long as the proper rate of flow is maintained. When the rate of flow drops below a predetermined value, the cup empties closing the electric contacts. This rings a bell to call the operator.

A slight modification which might produce better results is to extend the overflow tube down the outside of the cup to the bottom. This would provide the familiar effect of the Soxhlet extraction apparatus. The cup would fill with liquid until the top of the syphon is reached, then all the liquid would run out into the next cup. This intermittent filling and emptying of the cups would probably provide more thorough extraction of the chips.

B. Continuous Precipitation Unit

Dubrunfaut (44) (1869) presented a method for the separation of levulose as the calcium levulate. Many investigators have since attempted to improve on this method, but it continued until 1926 to be the most satisfactory means of isolating levulose. Dubrunfaut used 100 c.c. of sirup containing ten grams of previously inverted sugar and added six grams of powdered calcium hydroxide at a low temperature with stirring. The precipitate obtained by such a method is a finely divided suspension very difficult to filter and wash.

Jackson, Silsbee and Proffitt (45) (1926) contributed the first notable improvement in the original Dubrunfaut method. They give the following details of a typical method of procedure. "Six liters of the levulose-containing solution were con-

44. Dubrunfaut, op. cit., (Reference 10)
45. Jackson, Silsbee and Proffitt, op. cit., (Reference 5)

tained in a large cylindrical percolator, which was graduated in 100 c.c. divisions. The tubulature in the bottom was connected with the freezer (an ice cream freezer used as the reaction chamber) by a copper tube extending into the hole in the dasher. The flow of solution was regulated by a stopcock.

"The slaked lime was diluted with water to a volume of 1,050 c.c. and was added to the freezer in 15 portions of 70 c.c. each. One portion of lime was thus equivalent to 400 c.c. of sugar solution. About 500 c.c. of water and 1 portion of lime were introduced into the freezer and cooled by sparingly salted ice to a temperature of about 1 or 2°C. The levulose solution was then allowed to drip slowly into the mixture until 400 c.c. had been added. At this point another portion of lime was added, and the operation was continued in this manner until the entire amounts of the reactants had been introduced."

The investigators reported the filtration of cakes from ¾ to 1 inch in thickness in five to seven minutes, whereas experiments in this laboratory with the old method have required from fifteen to forty-five minutes for the formation of 1-inch cakes.

Altho the above method gives a somewhat granular precipitate which may be filtered satisfactorily, it is too laborious and time consuming when applied to a larger scale of operations. It was necessary to develop a method for the precipitation of

lime levulate that would produce a satisfactory precipitate and still be adaptable to commercial production.

A number of experiments were performed using different methods for combining the reactants, and it was found that a continuous addition of both reactants in the proper ratio, together with the continuous removal of the lime levulate suspension, gave the best results. The details of a typical experiment will be presented.

A clarified and hydrolyzed Jerusalem artichoke extract containing 10% solids, and a suspension of hydrated lime were allowed to flow slowly into a vessel with efficient stirring. The reactants were added in the ratio of 1 liter of extract to 200 c.c. of lime suspension. The reactants were introduced into the bottom of the container and the lime levulate suspension allowed to overflow at the top. The temperature of the reaction mixture was kept below $5^{\circ}C$. After the procedure had become continuous, filter cakes of $\frac{1}{8}$ inch thickness were deposited upon filters in 1 $\frac{1}{2}$ minutes. The first lime levulate filtered contained the seed which was prepared according to the method of Jackson and his associates, and required 13 minutes for the formation of a $\frac{1}{8}$ inch cake.

Other experiments which have been performed indicate that the method works well at room temperature, and it is possible that no refrigeration will be necessary.

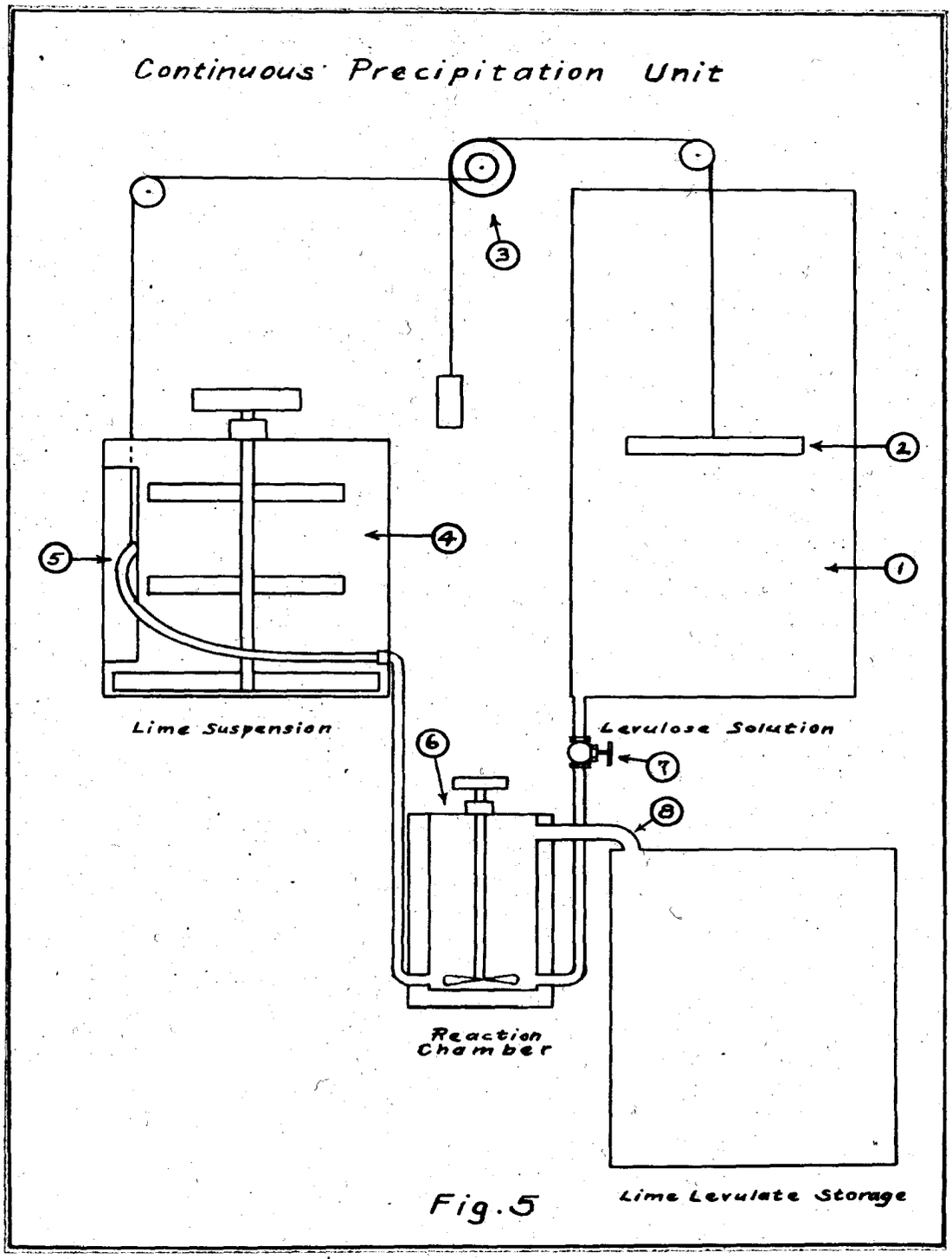
Continuous Precipitation Unit
3
2
1
4
5
Lime Suspension
Levulose Solution
6
7
8
Reaction Chamber
Lime Levulate Storage

Fig. 5

A diagramatic sketch of a continuous precipitation unit is presented. In Figure 5, 1 indicates a tank for the levulose solution, 4 is the lime suspension tank and 6 is the reaction chamber. The lime suspension tank is equipped with a large triple-bladed stirrer, while the reaction chamber contains a high-speed propeller agitator. A float, 2, is supported on the surface of the levulose solution and activates, by means of ropes and pulleys, an overflow pipe, 5, attached by a flexible hose to the kettle, 4. The mechanism, 3, consisting of pulleys of varying size makes it possible to vary the relative rate at which the overflow pipe, 5, is lowered in comparison with the change in level of the float, 2. The valve, 7, is adjusted to give any desired rate of flow for the sugar solution, the lime being added in the required ratio by the mechanical arrangement, 3, for lowering the overflow pipe, 5. The sugar solution and the lime suspension enter the precipitating chamber, 6, where they react to form the lime levulate in the presence of a predominating quantity of seed which offers an enormous area for crystal growth. The resulting precipitate is very granular and easy to filter and wash. As the reactants are added, the suspension of lime levulate overflows from the reaction chamber through the overflow pipe, 8, to a storage tank or to a continuous filter. The tanks and the reaction chamber may be jacketed if the precipitation is carried out at temperatures other than room temperature.

C. Carbonator

For laboratory scale experiments for the carbonation of lime levulate suspensions, it is satisfactory to bubble the gas through the suspension, which is kept in violent agitation by a stirring propeller. This procedure, however, is too wasteful of gas for large-scale operations.

A simple pressure carbonator is under construction with which we hope to be able to carbonate lime levulate suspensions conveniently and economically. The carbonator, as shown in Figure 6, consists of a 15-gallon galvanized iron expansion tank mounted on an axle shaft and supported in an iron frame. Pulleys are arranged so that the tank may be revolved during the carbonation process. Carbon dioxide is admitted through holes in the axle shaft, and the tank is kept under pressure during the process. The tank is filled and emptied through a valve located on one side near the end of the tank. A coil is built into the tank so that the contents may be heated by steam or cooled by cold water or brine, as required.

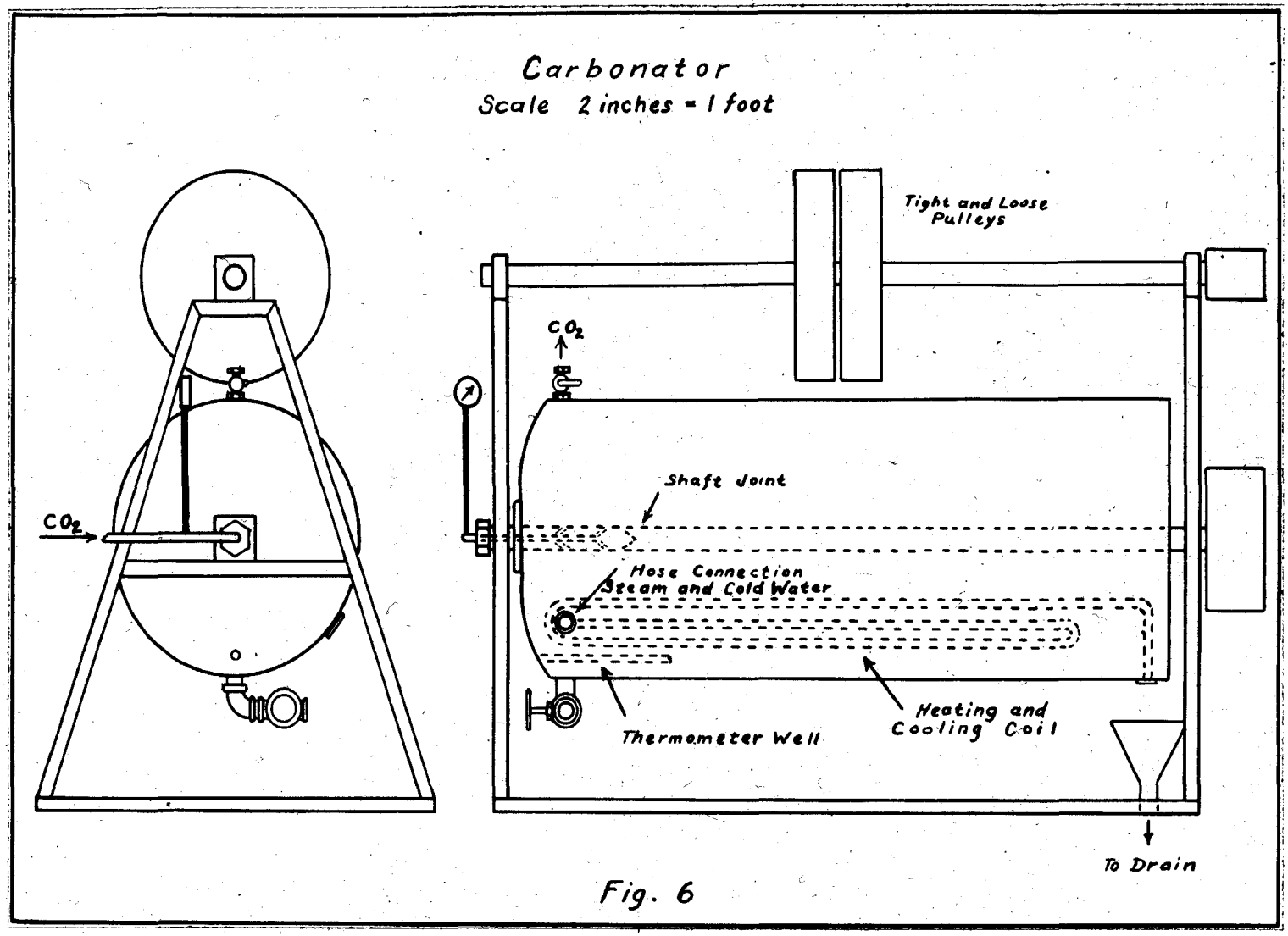
Carbonator
Scale 2 inches = 1 foot
Tight and Loose Pulleys
CO_2
CO_2
Shaft Joint
Hose Connection Steam and Cold Water
Thermometer Well
Heating and Cooling Coil
To Drain

Fig. 6

SUMMARY

The factors controlling the conversion reaction have been determined.

The decomposition of levulose under conditions of high acidity and temperature has been studied, and the limiting conditions have been determined.

Conversion experiments under varying conditions of concentration and acidity have been run, and the data are presented in the form of tables and graphs.

Normality-pH data for different concentrations of juice treated with varying quantities of sulfuric and hydrochloric acids have been determined.

A table has been prepared which shows the amount of sulfuric or hydrochloric acid required to convert a juice of any concentration from 4 to 40% total solids in one hour at 80°C. Sufficient data are presented to enable the calculation of similiar tables for different periods of time.

Details of the methods used for the desiccation of two and a half tons of Jerusalem artichoke tubers have been given. Possible improvements in the drying equipment have been presented.

Designs for several new pieces of equipment have been presented, including a continuous extraction unit, a continuous precipitation unit, and a carbonator.

Details of a new and improved process for the isolation of levulose as calcium levulate have been presented.